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Development of Sampling Method for Total Atmospheric Selenium

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DEVELOPMENT OF SAMPLING METHOD FOR TOTAL ATMOSPHERIC SELENIUM

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DEVELOPMENT OF SAMPLING METHOD FOR TOTAL ATMOSPHERIC SELENIUM

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PREFACE

Experimental work on this project began in July 1973 and was completed in June 1974.

M. Patricia Alewine, Associate Chemist, and Michael Rooks, Assistant Chemist, assisted in performing the work described in this report.

Discussions with members of the staff of the National Environmental Research Center at Research Triangle Park and with Dr. William Fulkerson and his associates at Oak Ridge National Laboratory were helpful in planning this work and in interpreting the results.

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SECTION I

INTRODUCTION

This report describes the experimentation undertaken and the results obtained in connection with a project to develop sampling and analytical methods for total atmospheric selenium. The primary purposes of this contract were to develop a collection technique for the quantitative collection of total atmospheric selenium and to characterize the forms in which selenium occurs in the atmosphere. A secondary, but essential, requirement was that an analytical method be selected and demonstrated to be suitable for the routine laboratory determination of the selenium in field-collected samples.

Although little is known about the occurrence, distribution, and concentration of selenium in the atmosphere, the element and its compounds may be as significant with regard to health as some others that have been more thoroughly investigated. Selenium compounds are known to be toxic, although their precise role in human biochemistry is not fully understood. A threshold limit value (TLV) of 0.2 mg/m^3 has been established for selenium compounds (as Se) by the American Conference of Governmental Industrial Hygienists.[1] Recognition of the possibility of increasing exposure of the populace to selenium from combustion and incineration processes demands that more attention be given to the methodology of sampling and characterization of atmospheric selenium.

Selenium is widely distributed in nature and occurs only in very small concentrations, most often in association with sulfide minerals. It is concentrated from soils in some areas by certain types of plants. Even in these more concentrated natural forms, however, the proportion of selenium is very low. The average concentration of selenium in the earth's crust has been estimated to be only about 0.09 µg/g (parts per million).

Major sources of atmospheric selenium include nonferrous metallurgical operations, glass-melting furnaces, the combustion of fossil fuels, and the incineration of solid wastes, especially paper.[2,3] It has been estimated that in 1969 the commercial consumption of selenium in the United States was 660 kkg (728 tons). Emissions to the atmosphere were estimated to total 900 kkg (986 tons); of this amount, 65% was derived from the burning of coal, 21% from glass-manufacturing processes, 9% from the production of nonferrous metals, and 7% from the burning of fuel oils.[4]

There appears to be no firm information in the literature on the chemical species in which selenium occurs in the ambient atmosphere. This lack of information may be attributed to the difficulties arising from the extremely low total concentration levels of selenium and to the fact that the selenium compounds that may be present can constitute no more than a small fraction of the total atmospheric contaminants in any given sample.

The approach undertaken relative to the sampling problem was based on the use of retentive filters for the collection of particulate material containing selenium and evaluations of chemically treated filters for retention of selenium that may occur in the gaseous or vapor form. In the initial phase of the investigation, laboratory aerosol generators were set up for evaluations of filter materials, and some effort was expended in establishing the 2,3-diaminonaphthalene (DAN) fluorometric method as the primary analytical technique for selenium. Later, samples of atmospheric particulate material were analyzed for selenium and procedures were investigated for determining the relative amounts of selenium present in different oxidation states in the particulate material. Also, additional selenium aerosol and vapor generators were set up, characterized, and used in evaluations of other candidate sampling devices.

SECTION II

SUMMARY

The primary purposes of this contract were to develop a technique for the quantitative collection of total atmospheric selenium and to characterize the forms in which selenium occurs in the atmosphere.

The approach undertaken relative to the sampling problem was based on the use of retentive filters for the collection of particulate material containing selenium and evaluations of chemically treated filters for the retention of selenium that may occur in the gaseous or vapor form. In the initial stages of the investigation, laboratory aerosol generators were set up for evaluations of filter materials and, on the basis of comparison with other methods, the 2,3-diaminonaphthalene (DAN) fluorometric method was selected as the primary analytical technique for selenium. Later, samples of atmospheric particulate matter were analyzed for selenium and procedures were investigated for determining the relative amounts of selenium present in different oxidation states in the particulate material. Also, additional selenium aerosol and vapor generators were set up, characterized, and used in evaluations of other candidate sampling devices.

It appeared that the selenium present in the ambient atmosphere exists predominantly as, or in association with, particulate matter, and that little or no loss of selenium by vaporization occurred during continuous sampling with filters. Thus, it was tentatively established that conventional particulate sampling was sufficient for collecting the bulk of atmospheric selenium. Vapor forms of selenium are believed to make a negligible contribution to total atmospheric selenium.

The most probable chemical forms in which atmospheric selenium exists were determined to be the element and the dioxide (or selenite).

SECTION III

CONCLUSIONS

On the basis of the experimental results presented in this report—primarily the results of laboratory experiments with a dry-selenium dioxide aerosol generator and the analyses of atmospheric particulate samples—the following conclusions were reached.

- Selenium occurs in the atmosphere primarily as selenium dioxide and elemental selenium, in roughly equal proportions. Selenium in the +6 oxidation state does not occur in the atmosphere. Efforts to establish the presence or absence of organic selenium were not conclusive.

- Selenium occurs in the atmosphere primarily in particulate form or in association with particulate material. The contribution of vapor forms to total atmospheric selenium is believed to be negligible.

- Little or no selenium is lost by vaporization during continuous sampling with filters.

- Selenium in the atmosphere is not primarily associated with the smaller size fractions, as it has been shown to be in stack emissions, but is most abundant in the particle sizes near the mass mean diameter.

- Conventional high-volume particulate sampling is adequate for the collection of atmospheric selenium.

- Of the reagent-impregnated filters evaluated for collecting vapor forms of selenium, none were demonstrated to be applicable to atmospheric sampling, and, moreover, they were not shown to be effective in laboratory experiments.

- Analyses of particulate samples collected at an urban site of heavy industrial pollution and samples collected at a site of only moderate pollution suggested that the selenium concentrations in the air at the two sites were the same—

essentially at a uniform background level—and that the sources in the heavily polluted area were not significant emitters of selenium.

- Errors can occur in the estimation of selenium concentrations by the DAN-fluorometric method if samples are subjected to a strong oxidative treatment without a subsequent reduction step to convert Se(VI) to Se(IV).

- Cyclohexane was found to be superior to toluene or hexane as the extracting solvent for a piazselenole, primarily because of the much lower blank fluorescence observed with cyclohexane.

SECTION IV

RECOMMENDATIONS

As a result of this investigation, several recommendations for future research can be made. First, additional laboratory studies should be conducted to evaluate treated filter materials for the retention of elemental selenium vapor. Studies such as these take on added significance in view of recent reports that selenium emissions from coal-fired power plants initially exist as elemental selenium vapor. It is reported that the sulfur dioxide present in the stack effluent is sufficient to insure the reduction of any selenium dioxide to the element. Also, the importance of these studies is underscored by the fact that coal burning represents the single most significant source of atmospheric selenium. To facilitate the experimental work, heated selenium metal (possibly in an inert atmosphere) should serve as a convenient source of the metallic vapor in a laboratory generator. Some effort should also be expended to answer several questions concerning the nature of the elemental selenium vapor: what is the allotropic form of the metal in the vapor phase?; what is the stability of the metal vapor with respect to oxidation or reduction in the atmosphere?; and does the selenium metal vapor tend to condense rapidly to form an aerosol? After these questions concerning the laboratory investigation are satisfactorily answered, sampling for selenium in the vicinity of a coal-fired power plant should be conducted.

Secondly, additional methods for sampling the volatile organic selenide—dimethyl selenide—should be considered. Sorption on an activated carbon surface with subsequent desorption, oxidation, and analysis is a potential avenue for future investigation. If this volatile selenide could be successfully sampled, its possible presence in the ambient atmosphere could then be investigated.

Finally, additional methods of selenium analysis which may offer increased sensitivity and specificity should be evaluated in greater depth. For example, the gas chromatographic methods briefly studied in this investigation should be reconsidered. These methods are based on the gas chromatographic separation of a piazselenole with subsequent detection by electron capture. An additional recently described gas chromatographic method which shows the promise of increased sensitivity and specificity involves the detection

of a piazselenole by microwave emission spectrometry (MES). Because the MES detector response is not a function of the organic moiety comprising the piazselenole but a function of the selenium atom itself, the method appears to offer a significant improvement over conventional electron capture detection of the piazselenole. For these reasons the GC-MES technique should also be considered for selenium determination in atmospheric samples.

SECTION V

METHODS FOR THE DETERMINATION OF SELENIUM

Because of the importance of establishing a convenient and reliable analytical method for selenium, three of the several methods presented in the literature were evaluated for their suitablity in the routine analysis of atmospheric samples. The three methods which appeared to be the most adaptable for the purposes of this study were the fluorometric procedure using DAN, a gas chromatographic method using DAN or either 4-chloro-o-phenylenediamine or 4-nitro-o-phenylenediamine, and a catalytic method based on the reduction of methylene blue. Although neutron activation analysis, atomic absorption spectrophotometry, and spark source mass spectrometry have seen a considerable amount of use recently for the determination of elements in atmospheric particulate material, they were not deemed especially suitable for the purposes of this project. However, a new, highly sensitive technique worthy of future consideration has been developed at the Oak Ridge National Laboratory.[5] This method for the determination of selenium is based on the gas chromatographic separation of a piazselenole with microwave emission spectrometric (MES) detection. The method appears to offer even more sensitivity than the methods considered in this study.

THE METHYLENE BLUE METHOD

The catalytic methylene blue method developed by West is a simple procedure involving no instrumentation and few reagents.[6] It is useful over a range of 0.1 to 1.0 µg of selenium. It has been used by West to determine selenium in smoke from trash burning,[7] and in cigarette papers, other papers, and tobacco.[8]

The method is based on the catalytic effect of trace amounts of selenium in the reduction of methylene blue by sodium sulfide. Ethylenediaminetetraacetic acid (EDTA) is used as a general masking agent, and formaldehyde, which suppresses the reducing power of sodium sulfide, is used to stabilize the blank. By taking advantage of the inducing effect of Fe(III), the limit of detection can be made as low as 0.1 µg of selenium.[6] Calibration data are obtained by measuring the time required for complete decolorization of methylene blue after mixing the reagents in the presence of known quantities of

selenium. A linear calibration curve is obtained by plotting the reciprocal of the time (min^{-1}) versus micrograms over the range of 0.1 to 1.0 µg of selenium.

In our evaluations of the methylene blue method, typical results were those obtained in an experiment involving the recovery of selenium from spiked glass-fiber filters by extraction with water. These results are presented in Table 1. This exercise demonstrated the uncertainty in the methylene blue method of analysis for amounts of selenium less than about 0.25 µg. Below this level, reproducibility suffered from the visual uncertainty in the color change at the end point. On the other hand, simultaneous determinations of selenium in identical samples by the DAN-fluorometric method resulted in selenium recoveries in excess of 90% of the theoretical (spiked) amount. Thus, the low recovery of selenium in the case of the methylene blue method suggested that the filters may contain a surface material that inhibits the catalytic effect of selenium on the reduction of methylene blue by sulfide. For these reasons, and specifically for the reason of limited sensitivity, the methylene blue method was not selected as the primary method of analysis for atmospheric selenium.

Table 1. RECOVERY OF SELENIUM FROM FILTERS WITH ANALYSIS BY THE METHYLENE BLUE METHOD

Amount of Se added, µg	Amount of Se recovered, µg
0.0	0.09
0.05	0.19
0.10	0.19
0.25	0.23
0.50	0.35
0.75	0.52
1.0	0.67

THE GAS CHROMATOGRAPHIC METHOD

The gas chromatographic method is relatively new. It was introduced by Nakashima and Tôei.[9] The compound 4-chloro-o-phenylenediamine reacts with selenious acid (Se(IV)) to form the 5-chloropiazselenole which is detectable by electron-capture gas chromatography. Later, Shimoishi and Tôei used 4-nitro-o-phenylenediamine to form 5-nitropiazselenole, which is more sensitive to electron-capture than the chloro

compound.[10] Shimoishi has used the gas chromatographic method to determine selenium in pure tellurium[11] and in sea water[12]. As little as 2 ng of selenium was detected by this method.

More recently an article by Young and Christian[13] further pointed out the utility of the gas chromatographic method of selenium analysis. In this example, selenium (IV) reacted with 2,3-diaminonaphthalene at pH 2 to form the well-established piazselenole, which was then extracted with hexane. An aliquot of the hexane layer was analyzed gas chromatographically with an electron-capture detector. As little as 0.5 ng of selenium could be detected; 10 ng of selenium could be determined in a sample by extracting into 0.1 ml of hexane and injecting a 5-µl aliquot of the extract. The method was applied to the determination of physiological amounts of selenium in human blood and urine. River water samples were also analyzed.

In our brief evaluation of the gas chromatographic methods, known selenium samples were analyzed by the methods of Young and Christian[13] and Shimoishi and Tôei.[10] In a slight modification of their procedures, cyclohexane was used as the extractant for the piazselenole rather than the hexane or toluene used by Young and Christian and Shimoishi and Tôei, respectively. From studies of the DAN-fluorometric method to be described later in this report, we found cyclohexane to be superior to hexane or toluene as the extracting solvent for a piazselenole, primarily because of the much lower blank observed with cyclohexane.

The minimum amount of selenium that could be detected in this evaluation of the GC methods was about 0.5 ng (per 5 µl injection). The method of Shimoishi,[12] in which 4-nitro-o-phenylenediamine is used as the reagent to form the piazselenole, was found to be somewhat more sensitive than the method using the DAN complex. Because Young and Christian[13] pointed out that the DAN complex was as sensitive to electron-capture detection as the 4,5-dichloropiazselenole of Nakashima and Tôei,[9] the present results suggest that the 5-nitropiazselenole is the most sensitive of the piazselenoles investigated thus far to electron-capture detection.

Although the 5-nitropiazselenole offered the most sensitivity, an effluent fraction that was observed in the blank produced a peak that overlapped the piazselenole peak and interfered with the measurement of peak area. A similar observation was made by Shimoishi[12] who removed the overlapping peak by washing the extract with hydrochloric acid solution. The possibility of back-extraction of the 5-nitropiazselenole into the

washing solution appeared to be no problem. It is conceivable that such a washing step would have removed the overlapping peak observed in our evaluation of the method.

THE DAN-FLUOROMETRIC METHOD

From the beginning of this project, we had planned to use the DAN-fluorometric method as the primary method for the determination of selenium. This selection was based principally on the fact that the DAN method had been chosen as a tentative standard method by the Intersociety Committee on Methods for Ambient Air Sampling and Analysis.[14] The essentials of this method were introduced in 1962 by Parker and Harvey.[15] The DAN method was shown to provide more sensitivity and convenience than the previously used 3,3'-diaminobenzidine method. Since that time, the DAN method has been used for the determination of selenium in many kinds of materials. The experimental procedure is straightforward, and the sensitivity limit has been variously reported to be 2 to 20 ng of selenium.

Because the DAN-fluorometric method was the primary method of selenium analysis used in this laboratory, the method will be given in some detail, incorporating the modifications developed during our experimentation.

> Routine atmospheric samples were collected on 20.3- by 25.4-cm (8- by 10-in.) glass-fiber filters in high-volume samplers. A 13- by 25-cm^2 section of the filter (cut into 6-cm^2 pieces) was cautiously extracted with 30 to 50 ml of a 10:1 mixture of concentrated nitric and perchloric acids. After boiling to reduce the volume to about 5 ml, the solution was diluted to approximately 50 ml with distilled water and the solution volume again reduced by boiling. The second digestion was then conducted with 5 to 10 ml of concentrated hydrochloric acid and the total volume reduced again.
>
> After appropriate treatment to dissolve the sample containing 0 to 1 µg of selenium, the solution was adjusted to pH 2 with successive additions of 10 N, 1 N, and 0.1 N NaOH. The resulting solution was then passed through a 25-ml buret filled to the 10-ml mark with regenerated Dowex 50 WX-8, 50- to 100-mesh cationic exchange resin at a flow rate of approximately 0.5 ml/min. The effluent was collected along with any remaining traces of selenium washed from the column with 25- or 30-ml of distilled water. To this solution was added 0.5 ml

of 0.1 M EDTA, 0.5 ml of 0.1 M NaF, and 5 ml of 0.1% DAN solution. (The DAN was dissolved in 0.1 N HCl to give a 0.1% solution that was stable under refrigeration for about 3 days.) The solution containing the selenium was then readjusted to pH 2, and an additional 5 ml of 0.1% DAN was added after which the solution was allowed to stand for 2 hr.

The solution was then transferred to a separatory funnel and the piazselenole was extracted into exactly 10 ml of cyclohexane by shaking for 0.5 min. After the separation of the aqueous and organic phases, the cyclohexane layer was filtered into a cuvette through a filter paper plug placed in the stem of the separatory funnel to remove droplets of water.

The fluorescence intensity of the sample was then measured at an exciting wavelength of 380 nm and a fluorescence wavelength of 525 nm. A solution containing 1.0 µg of selenium was used as the reference standard. When a filter fluorometer was employed, a Corning No. 5970 primary (uv) filter was used in conjunction with a Corning No. 4010 (maximum transmission at 525 nm) secondary filter. A linear calibration curve was observed over the range of 0 to 1 µg of selenium in 10 ml of cyclohexane.

In the procedure outlined above, the $HClO_4/HNO_3$ digestion was used to leach the selenium from the particulate material and to oxidize any selenium present as the element to Se(IV). It was determined that the +4 oxidation state, in solution as selenite (SeO_3^{-2}), was the only form of selenium appropriate for reaction with DAN to produce the fluorescent piazselenole. The HCl digestion ensured the reduction back to Se(IV) of any selenium present as Se(VI) or any that had been inadvertently oxidized to Se(VI). Experiments demonstrating the utility of the hydrochloric acid digestion are presented in Section VII of this report.

The dilution and reboiling of the solution after the initial $HNO_3/HClO_4$ digestion served to expel the dissolved oxides of nitrogen and thus prevented nitrite ion interference. The EDTA and NaF solutions were used as masking agents to reduce the possibility of metal ion interferences. Also, it was found that the results were not significantly affected by allowing the solutions to stand in a well-lighted laboratory for the prescribed 2-hr period.

By using cyclohexane as the extracting solvent rather than toluene as suggested in the Intersociety Committee method, we were able to lower the blank markedly and to increase reproducibility considerably. After correction for the blank value, samples containing as little as 0.01 µg of Se were analyzed. This detection limit represented almost an order of magnitude reduction due to the lower blank value in cyclohexane. The detection limit offered by this modification of the DAN-fluorometric method was as good as, or better than, the limits offered by the other methods of selenium analysis evaluated in this study.

As a further evaluation of the DAN-fluorometric method, a National Bureau of Standards Standard Reference Material was analyzed for selenium. This standard, "Trace Mercury in Coal" (SRM 1630), is not certified for selenium, but a value for selenium content of 2.1 µg/g (as Se) is included in the certificate as "information only". Our method of analysis of this coal sample was the usual DAN method with aqueous samples prepared by the Schöniger oxygen combustion-flask technique. The powdered coal samples were supported in the flask in quartz wool contained in a platinum mesh boat. The absorbing solution used in the Schöniger flask was 0.5 M HNO_3. Our analysis yielded a value for selenium content of 1.6 ± 0.4 µg/g. This value was not only lower than the reported value of 2.1 µg/g but the precision was not as high as was desired. Incomplete combustion of the samples could, in part, explain the low results and lack of precision because some samples were observed to have an insoluble tar-like residue remaining in the flask after removal of the absorbing liquid.

SECTION VI

LABORATORY GENERATION OF SELENIUM VAPORS AND AEROSOLS

From the outset it was recognized that assembling and establishing the performance of laboratory aerosol and vapor generators were of prime importance in the evaluation of candidate sampling devices. Thus, during the course of the investigation, we constructed and evaluated several selenium generating devices for use in the laboratory.

NEBULIZATION AEROSOL GENERATOR

The first device tested was a selenium aerosol generator based on a DeVilbiss No. 841 nebulizer. In this relatively simple system, the nebulizer was used to spray a solution prepared by dissolving elemental selenium in a small amount of nitric acid and diluting with water or a sodium or ammonium chloride solution to a known selenium concentration. This nebulizer was designed for inhalation therapy and is intended to produce particles in the size range from 1 to 10 μm when dilute aqueous solutions are dispersed from its 500-ml solution reservoir. Filtered and humidified air from the laboratory compressed air system was passed through the nebulizer at 2.5 l/min. The output of the nebulizer was diluted with clean compressed air at various dilution ratios. The relative humidity of the dilution air was controlled by mixing two dilution airstreams, one humidified and the other dried. The dilution chamber consisted of a 5.1-cm i.d. glass tube 51 cm long, with three sampling ports located at intervals along the tube. The dilution chamber was vented to a hood.

Table 2 shows some preliminary results obtained for the measured generator output at two selenium solution concentrations. The nebulizer solution was prepared for these tests by dissolving elemental selenium in dilute nitric acid and diluting with water. The aerosol was sampled for 2 hr at 2 l/min through a glass-fiber filter followed by a bubbler containing water. The glass-fiber filter was extracted with water and the selenium was determined by the methylene blue method. No selenium could be detected in the bubbler solution, indicating that most of it was collected on the filter in particulate form. The results of these analyses suggested that reasonably satisfactory performance of the generator system could be expected at an output concentration level of about 1 ng/l. With this technique, the concentration of

Table 2. NEBULIZATION-GENERATOR OUTPUT

Concn of Se in nebulizer solution, mg/l	Flow rate of dilution air, l/min	Dilution[a] factor	Concn of Se in generator output, ng/l
100	2.0	0.8	140
	6.0	2.4	110
	10.0	4.0	40
1	6.0	2.4	0.6
	6.0	2.4	0.8

[a]The flow rate of air through the nebulizer was 2.5 l/min.

aerosol produced approached the practical limit that could be measured by the analytical method within a reasonable sampling time.

Although it was possible to evaluate field sample-collection devices at the 1 ng/l concentration level, it was desirable to work at lower levels more nearly approaching those that are expected to occur in the atmosphere. We therefore conducted some preliminary experiments with nebulizer solutions containing a relatively high ratio of a soluble salt to dissolved selenium. The principle was based on the assumption that the ratio of the salt to selenium would be the same in the aerosol particles as in the nebulizer solution, and that determination of the concentration of the salt in the aerosol would permit a valid estimation of the concentration of selenium when the selenium was too low to be measured by the most sensitive analytical method. To test this principle, we nebulized a solution containing 1 mg/l of selenium and 10 g/l of ammonium chloride. The aerosol was diluted and sampled on a glass-fiber filter, as in previous experiments. The selenium content of the filter was determined by the methylene blue method and the ammonium content was determined by the ammonia electrode method. The calculated weight ratio of ammonia (NH_3) to selenium (Se) in the nebulizer solution was 3.4×10^3, and the ratio found by analysis of the generator output was 4.3×10^3. In a similar experiment in which sodium chloride was used instead of ammonium chloride and the chloride content of the aerosol was determined, much poorer agreement was obtained.

In additional experiments we substituted ammonium sulfate for ammonium chloride in the nebulizer solution since the sulfate is a widely occurring constituent of atmospheric aerosols. The nebulizer solutions were prepared to contain 0.01% of selenium (as Se) and 1.0% of NH_3 added as ammonium sulfate, a

ratio of NH_3 to Se of 100 to 1. Analyses of the aerosol collected on a glass-fiber filter gave ratios of NH_3 to Se averaging about 50 to 1. In one set of experiments, filters were extracted with a measured volume of water and aliquots were taken for determinations of ammonia by the Nessler method and for determinations of selenium by both the DAN-fluorometric and methylene blue methods. The two methods for selenium gave approximately the same average value for the concentration of selenium in the aerosol, about 140 ng/l, but the precision of the measurements was poor. Some of the variability of the results could have been attributable to instability of the aerosol generation or to variations in efficiency of sampling.

Results from further experiments on this principle of low-level selenium estimation in laboratory-generated aerosols proved to be inconsistent and widely variable. Also, the ratios of NH_3 to Se found in the aerosol seldom agreed with the known ratios in the nebulizer solution. At this point this technique was tentatively abandoned in favor of conducting sampling evaluations at selenium aerosol concentration levels sufficient for direct determination by existing techniques.

DRY-SELENIUM DIOXIDE AEROSOL GENERATOR

One form in which selenium is likely to occur in the atmosphere is selenium dioxide. Selenium dioxide could occur as solid particles or as the vapor, or in an adsorbed state in association with other particulate matter. It is possible, also, that selenium present in source emissions as the dioxide might be converted in the atmosphere to selenious acid or to another chemical form.

Thus, we set out to determine if dry selenium dioxide could be used as a laboratory source of selenium vapor or particulate material. As a starting point, it was of interest to estimate the volatility of selenium dioxide at ambient temperatures. From published data on the vapor pressure at several temperatures,[16] it was calculated that the volatility at 25°C is about 10^5 ng/m^3. This value is several orders of magnitude higher than any reported atmospheric concentration of selenium, and it suggested that dry selenium dioxide might be a convenient source of selenium in the vapor form.

In a preliminary experiment to examine the practical significance of the volatility, we placed 100 mg of selenium dioxide between two glass-fiber filters and passed air at room temperature through the filters at 2.0 l/min, collecting samples of the effluent air in bubblers containing water. From the

volatility data, as much as 2 μg of selenium dioxide was expected in a 20-liter sample. However, no selenium could be detected in the bubbler solutions by the methylene blue method.

In later experiments a more elaborate set-up was constructed to employ dry selenium dioxide as a laboratory source of selenium. The dry-selenium dioxide generator was prepared by mixing an aqueous solution of selenium dioxide and an inert solid support, Chromosorb W, and evaporating the resulting mixture to dryness. The dry charge of SeO_2/Chromosorb W was then placed in a suitable glass column and enclosed by glass-wool plugs. Provisions for temperature control were made by wrapping the column with an insulated heating tape connected to a variable voltage source. For generation of selenium a dry airstream was passed through the packed column at a fixed rate and the effluent was sampled directly to determine its selenium concentration.

In an effort to characterize the form in which the selenium existed and its concentration in the effluent of the generator described above, several combinations of untreated glass-fiber filters and midget impinger bubblers containing distilled water were used for sampling. Typical results of the selenium analyses for the various sampling configurations are presented in Tables 3 and 4. The results are given in terms of the amount of selenium in nanograms removed by a given sampling device per liter of generator effluent sampled. Table 3 contains data obtained with a generator effluent temperature of 74°C as measured at the glass-wool plug in the end of the packed column. Table 4 contains data for an effluent temperature of 27°C (room temperature).

Table 3. SELENIUM ANALYSES OF GENERATOR EFFLUENT AT 74°C

Sampling medium	Se collected per liter of effluent sampled, ng
Glass-fiber filter	33
Second filter in tandem filters	1
Impinger bubbler (water)	10
Second bubbler in tandem bubblers	5
Filter following two bubblers	1
Bubbler following a single filter	0.5

Table 4. SELENIUM ANALYSES OF GENERATOR EFFLUENT AT 27°C

Sampling medium	Se collected per liter of effluent sampled, ng
Glass-fiber filter	1.2
Second filter in tandem filters	0.05
Impinger bubbler (water)	0.7
Filter following a single bubbler	0.02

The results with two glass-fiber filters in series indicated that the single untreated glass-fiber filter removed the selenium from the generator effluent with more than 90% efficiency. However, the impinger bubbler containing distilled water operated with only about 30 to 60% efficiency, depending upon the effluent temperature. One anomalous result was the unexpected low values for selenium retained on filters following bubblers. The filters were expected to retain the selenium passed by the bubblers, since a low efficiency had been found for the bubblers and a high efficiency for the filters. It may have been that losses occurred in the sampling train between the bubblers and the filters due to the large increase in the humidity of the sample airstream after passage through the bubblers.

From the results of preliminary experiments conducted with this type of selenium generator, it was concluded that the selenium did not exist primarily as a vapor of selenium dioxide or selenious acid, as expected from vapor pressure data, but as a particulate aerosol. Additionally, it was determined that the total selenium concentration of the generator aerosol was only about 2% of the selenium concentration expected in the gas phase as calculated from equilibrium vapor pressure data.

To further characterize the generator effluent, an Andersen "Mini Personnel" cascade impactor was employed for the purpose of approximate sizing of the particulate aerosol. This particular Andersen impactor provided four impaction stages and a final filter. To utilize the impactor, the generator effluent was routed to a large glass jug which provided the sampling environment and served as an enclosure for the impaction device. Several samples were taken from the generator operating at both room temperature and 74°C under conditions similar to those described earlier. With the generator

operating at room temperature, the initial sample volume of approximately 2 m^3 surprisingly yielded negligible amounts of selenium, i.e., less than 20 ng. Results from previous experiments in which the effluent was sampled with filters and bubblers directly from the generator at room temperature suggested that a 2-m^3 sample should yield a total of selenium in excess of 2 µg. However, with the generator operating at 74°C, higher concentrations were obtained although these results were lower than expected in view of earlier experiments involving sampling directly from the heated generator. Average results of the particle-size distribution for the effluent aerosol generated at 74°C are given in Table 5 for sample volumes of 2 to 8 m^3. The analyses for selenium on the impactor stages were done by the DAN-fluorometric method with the Turner filter fluorometer.

Table 5. PARTICLE-SIZE DISTRIBUTION OF SELENIUM AEROSOL GENERATOR EFFLUENT

Impactor stage	Particle size,[a] µm	Se,[b] %
First	>3.2	18
Second	3.2 to 2.3	10
Third	2.3 to 1.4	9
Fourth	1.4 to 0.43	6
Final filter	<0.43	57

[a]These size cuts were based on an assumed particle density of 3 g/cm^3.

[b]These average percentages of Se per stage were based on sample volumes of 2 to 8 m^3 with an average total Se concentration of 1.7 $µg/m^3$.

Because of the negligible amount of selenium collected with the generator operating at room temperature and the reduced amount collected with the generator heated to 74°C, it was suspected that a significant amount of selenium was lost in the tubing connections between the generator output and the enclosure for the impactor. However, the results of the particle-size analysis appeared to substantiate the results of analyses involving the sampling devices described previously. Efficiencies of distilled-water bubblers for removing selenium from the generator effluent were found to be 30 to 60% while untreated glass-fiber filters provided efficiencies in excess of 90%. In view of the significant percentage (>50%) of aerosol particles found to be smaller than 0.5 µm, it is reasonable to assume that most of these small particles

were not retained in the midget impinger bubblers and, hence, the analyses of the bubbler solutions could be expected to be low. However, glass-fiber filters appeared to collect the small particles efficiently and, thus, as the results indicated, yielded efficiencies in excess of 90%. In addition, the apparent dependence of bubbler efficiency on generator temperature pointed out in previous experiments can be rationalized on the basis of these results. If it is assumed that heating the generator gave rise to enrichment of the smaller particles, i.e., less than 0.5 to 1.0 μm, then bubbler efficiencies would be expected to decrease with this small particle enrichment; this assumption concurred with experimental observation.

The usual cumulative distribution plots of percent accumulation in the size cuts versus logarithm of the aerodynamic particle size were made for the data from the impactor analyses. The curve shapes suggested the possibility of a bimodal distribution. Although data are lacking for the large percentage of particles below 0.4 μm, the particle distribution appeared to have two maxima (MMD), one below 0.4 μm and one above 2 μm.

DIMETHYL SELENIDE VAPOR GENERATOR

For the evaluation of treated filter materials for their selenium retention properties, a known source of selenium vapor (with no particulate selenium) was required. For this purpose the diluted vapor of a liquid organic compound, dimethyl selenide, was used. This particular organic selenium compound was chosen not only for its volatility (bp = 58.2°C) and stability, but also for its biological significance. The expiration of dimethyl selenide into the atmosphere can result from plant and animal metabolism of ingested selenium compounds.[17,18]

The source of the dimethyl selenide vapor was a 100-liter Mylar bag to which a small volume (25 μl) of a dilute solution (1.38 mg/ml) of dimethyl selenide in methanol was added during the process of filling the bag with air. The resulting concentration of selenium (as Se) in the bag was 250 ng/l. Various candidate sampling devices were subsequently evaluated by sampling the contents of the Mylar bag directly.

SECTION VII

LABORATORY EVALUATION OF METHODS OF SAMPLING FOR SELENIUM IN AIR

In evaluating candidate sampling materials for their selenium retention properties, the approach was based on the use of retentive filters for the collection of selenium occurring in particulate form and chemically treated filters for the collection of selenium occurring in gaseous or vapor form. Although several reagent solutions were evaluated for use in impinger bubblers, the conception of the most appropriate sampling device for field use was a single reagent-impregnated fibrous filter for collection of total atmospheric selenium.

EVALUATION OF TREATED AND UNTREATED FILTERS

In the initial phases of the study, we investigated the efficiency of extraction of small amounts of selenium from Gelman Type A glass-fiber filters to which had been added known quantities of a standard selenium dioxide solution. On extraction of the filters with either water or a mixture of nitric and perchloric acids, an amount in excess of about 80% of the added selenium was routinely recovered. The solutions were analyzed by the DAN-fluorometric method as outlined previously. In one set of analyses, the nitric-perchloric acid extracts were passed through the ion-exchange column as suggested in the Intersociety Committee Method. Initially, losses of selenium in the column were found to be as large as 25%, but further experimentation with more efficient column washing demonstrated the losses to be usually no larger than 10%. Also, it was determined that the filter material itself was not a source of interference in the selenium determinations. That is, any contribution of selenium from the glass-fiber material was negligible or below the detectable limit.

Subsequently, several experiments were conducted to determine the selenium collection efficiency of glass-fiber filters, cellulose-fiber filters, membrane filters, and glass-fiber filters impregnated with one of three reagents. The reagents included lead acetate and two reducing agents—sodium sulfite and ascorbic acid—that are known to reduce Se(IV) to elemental selenium.

These particular experiments were conducted with the selenium aerosol generator, described previously, that was based on the nebulization of selenium dioxide solutions. It was

assumed that the aerosol particles formed consisted initially of selenious acid, with more or less associated water and a small proportion of excess nitric acid (the selenium dioxide in the nebulizer was in dilute nitric acid solution). It was also assumed that after evaporation of the solvent, the particles were relatively small, perhaps mostly submicron in size, although the size distribution for this aerosol generator was not determined.

Thus, glass-fiber filters (Gelman Type A) and Millipore filters (0.8-μm pore size) were compared for their retention of aerosol particles from the selenium aerosol generator. The nebulizer solution containing 0.01% selenium (as Se) was prepared by dissolving elemental selenium in dilute nitric acid. First, it was shown that known amounts of standard selenious acid solutions added to either type of filter were essentially completely recovered (80%, or more) by extraction with either water or a nitric-perchloric acid mixture. The output of the aerosol generator was sampled on 2.54-cm diameter filters at 2 l/min for 10 min. The filters were extracted with the acid mixture and analyzed by the DAN-fluorometric method. The glass-fiber filters appeared to be about twice as effective as the Millipore filters in retaining the aerosol particles. The significance of this result was uncertain since the particle-size distribution of the nebulizer aerosol was not established; however, it did suggest that a sizable proportion of the aerosol particles were submicron in size, as had been previously assumed.

Cellulose-fiber filters (Whatman No. 42) were also compared with glass-fiber filters for sampling the output of the generator. Concentration values (0.03 μg/l) calculated from determination of selenium collected on the cellulose-fiber filters were only about 25% of the concentration values found with glass-fiber filters (0.12 μg/l). Both types of filters were extracted with dilute nitric acid. The reason for this unexpected large difference was not clear. However, the results of these determinations, unlike most of the results that follow for the impregnated filters, were consistent and reproducible.

The experiments with impregnated filters were generally less than satisfactory because of the lack of reproducibility of the results. The poor reproducibility seemed to be most likely caused by difficulties in controlling the output of the nebulizer. There were, however, indications that the reducing agents, sodium sulfite and ascorbic acid, may have brought about some reduction of selenious acid to elemental selenium. The amounts of selenium found on these filters by extraction with water and determination by the DAN-fluorometric method were consistently lower than the amounts

found on unimpregnated glass-fiber filters, indicating that some of the selenium was in a water-insoluble form. However, the results calculated as concentration of selenium in the generator output were not reproducible.

There was evidence, also, that lead acetate in the filters may have reacted with the selenious acid (or selenium dioxide) in the generator output to form a water-insoluble product. Concentration values calculated from analyses of the filters were in some instances lower for lead acetate-impregnated filters extracted with water than for filters extracted with dilute nitric acid. This result suggested that an acid-soluble but water-insoluble product may have been formed. Also, a small amount of selenious acid added directly to a lead acetate-impregnated filter was not recovered by subsequent extraction with water.

Treated filters were evaluated also by sampling the effluent of the dry-SeO_2 generator that was described earlier in this report. Glass-fiber filters were treated with special solutions of silver nitrate in one case and lead acetate in another. The treatment solutions were essentially those described by Natusch et al.[19] for treatment of filter materials for the collection of hydrogen sulfide. All treated filters were used as back-up filters in tandem arrangements with untreated glass-fiber filters. The results of the preliminary experiments were somewhat encouraging; these results are shown in Table 6. The data indicated that the first untreated filter consistently removed the selenium present in particulate form, and that the untreated and lead acetate-treated back-up filters essentially collected no additional selenium. However, the $AgNO_3$-treated back-up filter appeared to collect an amount of selenium in excess of the amount in particulate form retained on the first filter. This tentative result for the silver nitrate-treated filter suggested that such a treated filter might be useful for retention of selenium present in the ambient atmosphere in the vapor form. Also, these data suggested that the dry-selenium dioxide generator was producing an effluent consisting of selenium dioxide in both the vapor and particulate forms, contrary to other indications that the selenium dioxide was essentially all particulate (see p. 17).

However, after additional experiments of a more diagnostic nature were conducted, the favorable results first obtained with the silver nitrate-treated filters were found to be subject to much uncertainty. The fluorescence readings obtained for blank silver nitrate-treated filters proved to be highly variable. Indeed, results obtained with silver nitrate-treated filters using the dry-selenium dioxide generator as the source of selenium yielded efficiencies from less than

Table 6. SELENIUM RETENTION OF TREATED FILTERS FOR SAMPLING THE DRY-SeO_2 GENERATOR EFFLUENT (PRELIMINARY RESULTS)

Glass-fiber filter treatment	Se retention (ng/l of generator effluent)
First untreated filter	1.25
Second untreated filter	<0.1
First untreated filter	1.25
Second $Pb(OAc)_2$ filter	<0.1
First untreated filter	1.25
Second $AgNO_3$ filter	1.45

10% to about 70% for selenium retention relative to the first untreated filter in a tandem arrangement. After several such analyses, it was concluded that the silver nitrate-treated filters possessed little, if any, reproducible selenium-retention capability. A similar result was obtained for silver nitrate-treated filters used in sampling a dilute vapor of the organic selenium compound, dimethyl selenide. The 250-ng/l vapor source of selenium used in these evaluations was the Mylar dilution bag described earlier. The resulting retention efficiencies of the treated and untreated filters for dimethyl selenide vapor were essentially the same and typically less than 5%.

In view of the latter results, it appeared that the initial conclusions concerning the nature of the effluent from the dry-selenium dioxide generator were appropriate. That is, no definitive evidence was found to suggest that the selenium present in the generator effluent was in any form other than particulate.

EVALUATION OF ACTIVATED CARBON

Sorbent tubes containing activated carbon were also used in an effort to collect dimethyl selenide vapor from the Mylar dilution bag. (The activated carbon was obtained from Mine Safety Appliances Company and was the product approved by the National Institute for Occupational Safety and Health for sampling organic vapors.) However, DAN analyses of samples obtained in this manner indicated selenium retention efficiencies typically less than 5%. In these experiments, distilled water was used to desorb the dimethyl selenide from the carbon. The low result did not necessarily mean that the

dimethyl selenide vapor was collected on the carbon with low efficiency, but it may have been that the overall recovery process of desorbing and analyzing the selenide had a low efficiency. This conclusion was supported in part by the work of Lewis et al.[20] on the collection of volatile selenium compounds expired from plants. These authors demonstrated by using Se^{75} in radiotracer experiments that activated carbon was effective in retaining volatile selenium compounds. In addition they found distilled water and 50% aqueous ethanol to be greater than 90% effective in desorbing the volatile selenium compound from the carbon. In light of the fact that our sampling efficiencies were very low with essentially the same sampling technique, it is probable that after desorption the selenide was not efficiently oxidized to the +4 oxidation state that is necessary for reaction with the DAN in the analytical procedure. The results were essentially the same, very low, even when the samples were digested in the mixture of oxidizing acids, nitric and perchloric. However, uncertainties in the digestion treatment included possible losses of dimethyl selenide by volatilization.

EVALUATION OF BUBBLERS

Because experiments using treated filters, untreated filters, and activated carbon for sampling the vapor of dimethyl selenide were essentially unsuccessful, subsequent experiments employed bubblers containing water, dilute nitric acid, or lead acetate solution for trapping the vapor. These experiments were essentially no more successful than earlier experiments; however, a few meaningful conclusions were drawn from these experiments with bubblers.

As the data in Table 7 demonstrate, the bubbler solutions that were digested with an oxidizing acid mixture consistently had higher values for selenium collection efficiency compared to the undigested samples, even though all efficiencies were low. The percent efficiencies were based on a 5-min sample at a 1 l/min flow rate from a selenium source of 250 ng/l or a total theoretical sample of 1.25 µg of selenium. The solutions from the bubblers were analyzed by the usual DAN method and, although the differences in the percent efficiencies of the digested and undigested samples appeared small, the differences were experimentally significant.

These data suggested that, although the results with the different bubbler solutions were similar, a bubbler could possibly be used for sampling dimethyl selenide with subsequent digestion with an oxidizing acid and analysis by the DAN method. The low yields in these experiments were also

Table 7. COLLECTION EFFICIENCIES OF BUBBLER SOLUTIONS FOR $(CH_3)_2Se$ VAPOR

Bubbler solution	Digestion step	Efficiency, %
H_2O	$HNO_3/HClO_4$	8
1 N HNO_3	$HNO_3/HClO_4$	8
2% $Pb(OAc)_2$	$HNO_3/HClO_4$	8
H_2O	None	2
1 N HNO_3	None	3
2% $Pb(OAc)_2$	None	1

probably due to losses of dimethyl selenide through its volatility and the inefficient oxidation of dimethyl selenide to the +4 oxidation state necessary for DAN analysis.

These results also paralleled those of Lewis et al.[20] in their radiotracer evaluations of bubbler solutions for sampling volatile selenium compounds. They were not able to retain significant amounts of selenium in a variety of liquid media: aqueous solutions of EDTA, KOH, NH_4OH, lead acetate, and $KMnO_4$-KOH; sodium ethylate in ethanol; the organic solvent, benzene; and diaminobenzidine (DAB) in hydrochloric acid solution.

The choice of the appropriate oxidizing conditions to effect the necessary oxidation of selenide to selenite on a filter or in a bubbler is not a straightforward matter. However, such an oxidation would be necessary for the analysis of a volatile selenide by the DAN method. Dimethyl selenide is oxidized to dimethyl selenoxide by the common strong oxidizing agents and to dimethyl selenide dihalide by active halogen oxidizing agents. Neither of these compounds is likely to react in significant yields with DAN in the fluorometric method of analysis. The yield of the reaction of these compounds, or dimethyl selenide itself, with the oxidizing digestion acids to give Se(IV) would also be expected to be low. Thus, the efficient reaction of dimethyl selenide on a reagent-impregnated filter surface to give Se(IV) for DAN analysis does not appear feasible. However, the trapping of a volatile selenium compound on a solid sorbent with oxidation and analysis at a later time appears to be an avenue for further investigation.

In conjunction with the evaluation of bubbler solutions for the retention of dimethyl selenide vapor, bubbler solutions were also tested for retention of selenium in particulate form. Using the effluent of the dry-selenium dioxide

generator, evaluations were conducted on aqueous bubbler solutions containing 10% lead acetate (suggested by the work of Pillay et al.[21]), 2% $AgNO_3$, 0.1 M HNO_3, or distilled water. The results of the selenium analyses conducted on these bubbler solutions after exposure to the generator effluent are presented in Table 8. The most significant result appeared to be the high efficiency of the dilute nitric acid bubbler relative to the others. Also, it was significant that the lead acetate bubbler performed poorly. These results suggested that a dilute acid solution would be most appropriate for use in a back-up bubbler for the sampling of ambient atmosphere for selenium.

Table 8. RETENTION OF SELENIUM FROM THE DRY-SeO_2 GENERATOR BY VARIOUS BUBBLER SOLUTIONS

Bubbler solution	Concn of Se in generator effluent, as indicated by analysis of the bubbler solutions, ng/l
Distilled H_2O	3.8
0.1 M HNO_3	5.6
2% $AgNO_3$	1.2
10% $Pb(OAc)_2$	<0.2

SECTION VIII

SELENIUM SAMPLING OF THE AMBIENT ATMOSPHERE AND INVESTIGATION OF THE CHEMICAL FORMS OF ATMOSPHERIC SELENIUM

In a preliminary evaluation of the Intersociety Committee DAN procedure for analysis of atmospheric particulate material, 25-hr samples were collected on glass-fiber filters in a high-volume sampler and were briefly digested with nitric and perchloric acids and analyzed. Values for selenium concentrations of 4.6, 5.1, 3.9, and 6.8 ng/m^3 were obtained at various times. These results were similar to those reported in the literature for selenium concentrations found in other parts of the country. Pillay, for example, found concentrations of total selenium in the range of 3 to 9 ng/m^3.[21] Others have found similar small concentrations.[22-26]

WATER-SOLUBLE AND WATER-INSOLUBLE SELENIUM IN PARTICULATE MATERIAL

The analysis of atmospheric particulate samples was explored further on other occasions. Samples from the ambient atmosphere outside the laboratory were collected on 20.3- by 25.4-cm (8- by 10-in.) glass-fiber filters with a high-volume sampler. One sample was cut into several squares of known area. Individual squares were extracted with either water or a mixture of nitric and perchloric acids. Prior to analysis by the DAN-fluorometric method, some of the extracts were passed through an ion-exchange column to remove impurities and others were not. Water extracts analyzed directly without the ion-exchange treatment showed strong effects of interferences and did not give the normal fluorescence spectrum of the DAN piazselenole. Water extracts treated by ion-exchange gave more nearly normal spectra, showing the effects of removing interfering substances. A blank portion of the filter extracted with water gave a normal low relative fluorescence intensity, indicating that the interfering substances were present in the atmospheric particulate material and not in the filter material. The atmospheric concentration of selenium estimated from these results for this particular sample was 0.36 ng/m^3.

Acid extracts analyzed directly without the ion-exchange treatment gave more nearly normal spectra than the water extracts and an estimated selenium concentration value of

0.93 ng/m³. With the ion-exchange treatment, a concentration value of 0.65 ng/m³ was obtained. Previous results with standard solutions of selenious acid indicated that as much as 25% of the selenium could be lost in the ion-exchange treatment if extreme care were not exercised.

The results of these experiments indicated that a portion of the selenium in the atmospheric particulate material was soluble in water and that acid treatment was required for the dissolution of a substantial additional portion. Thus, the selenium apparently occurred in at least two different states of chemical combination. These forms of particulate selenium were most probably selenium dioxide (or selenious acid depending on the amount of moisture present) and elemental selenium. The selenium dioxide (or selenious acid) would have been readily soluble in water yielding Se(IV) in solution, but elemental selenium would have required acid dissolution to give Se(IV) in solution for reaction with DAN. If it is assumed that the element and the dioxide were the only chemical forms of particulate selenium, as the data indicate, then it can be tentatively concluded from the analyses that each contributed approximately equally to the total selenium associated with the particulate material.

ATMOSPHERIC SAMPLING WITH FILTERS AND BUBBLERS

In additional experiments, untreated glass-fiber filters and distilled-water bubblers of the gas-dispersion type were employed for collecting ambient air samples. The samples were taken over a 6-day period within a laboratory open to a continuous flow of ambient air. During this period the average total particulate concentration was determined to be approximately 60 µg/m³. The sample volumes ranged from 43 to 51 m³. All samples were treated with a moderate $HNO_3/HClO_4$ (10:1) digestion step prior to routine analysis. Results of the DAN-fluorometric analyses for the selenium content of these atmospheric samples are presented in Table 9. These results, in general, paralleled those obtained with the dry-SeO_2 generator; however, the high value for selenium retained on glass-fiber filters following the distilled-water bubblers was unexpected. It could be that the conditions of high humidity following the bubblers contributed to the increased efficiency of the glass-fiber filters for removal of atmospheric selenium. Consequently, this particular result was in contrast to results of similar experiments conducted with the dry-selenium dioxide generator. In those experiments filters following bubblers retained relatively small amounts of selenium even though the bubbler efficiency was low.

Table 9. SELENIUM CONTENT OF AMBIENT ATMOSPHERIC SAMPLES

Sampling medium	Se found, ng/m^3
Glass-fiber filter	1.2
Second filter in tandem filters	0.2[a]
Distilled water bubbler	0.7
Filter following a bubbler	2.3
Second filter in tandem filters	0.7

[a]This value is uncertain because of its proximity to the blank.

SELENIUM ANALYSIS OF SIZED ATMOSPHERIC PARTICULATE MATERIAL

From the data in Table 9, the total atmospheric selenium concentration during this particular sampling period was estimated to be 3 ng/m^3. The selenium content of the particulate matter was estimated by analysis to be 20 µg/g. These results agree favorably with similar analyses reported in the literature. In particular, a recent publication by Natusch et al.[27] suggested that several toxic elements, including selenium, were preferentially concentrated into the smallest airborne particles of fly ash derived from coal-fired power plants. Natusch's selenium analyses by atomic absorption spectrometry ranged from 11 to 59 µg/g for airborne fly-ash particle sizes from 11.3 to 1.1 µm, respectively.

A similar experiment was conducted in this laboratory to determine whether or not such a preferential concentration of selenium in small particles exists for ambient atmospheric particulate matter. To facilitate this study we employed an Andersen cascade impactor which provided nine size cuts (eight stages and a final filter) over a particle-size range of 0.4 to 10 µm. The particulate matter on each stage was weighed and analyzed for selenium in the usual manner. Table 10 shows the results of the measurements. During the sampling period the average total particulate concentration was approximately 41 µg/m^3 for a sample volume of 700 m^3. The particle-size distribution was found to be log-normal with a mass median diameter (MMD) of approximately 1 µm. Although the results of the selenium analyses appeared somewhat uncertain because of the low value for the 0.95-to-1.8 µm size cut, one can conclude that this experiment was not positive evidence for the phenomenon of preferential concentration of selenium into the smaller particles (<0.5 µm) of the

Table 10. ANDERSEN CASCADE IMPACTOR SAMPLING OF THE AMBIENT ATMOSPHERE

Stage	Size,[a] μm	Particulate weight per stage (% of total)	Se content per stage (% of total)
0	>10	10.5	<5
1	6.4 to 10	7.2	<5
2	4.3 to 6.4	6.5	<5
3	2.9 to 4.3	7.2	<5
4	1.8 to 2.9	9.2	35
5	0.95 to 1.8	11.2	<5[b]
6	0.57 to 0.95	11.8	40
7	0.38 to 0.57	19.7	7
Filter	<0.38	16.5	<5

[a]The flow rate was 25 l/min at 25°C for these size cuts.
[b]This result is uncertain.

ambient atmospheric aerosol. In contrast to the preferential concentration phenomenon as cited by Natusch,[27] the present results tentatively suggest that the selenium in a multisource atmospheric aerosol may be most abundant in particle sizes close to the MMD.

BACKGROUND LEVEL OF ATMOSPHERIC SELENIUM

Other analyses of high-volume atmospheric samples revealed a significant difference between the selenium content of the particulate material in a heavy industry area and that in a less polluted area. An air sample taken in an area of moderate particulate concentration (on the Institute premises) was found to have a selenium content corresponding to 2.0 ng/m^3. The average total particulate concentration of this sample was 44 μg/m^3. From these figures the selenium content of the particulate matter was calculated to be 47 μg/g. However, analysis of a sample taken in an area of heavy industry (North Birmingham) gave a result of 2.6 ng/m^3 for selenium concentration when the average particulate concentration was 350 μg/m^3. These figures suggested an average selenium content of 7.4 μg/g in the ambient particulate matter in this area. Thus, it appears that the industry in this area of high particulate pollution is not a source of atmospheric selenium. It is probable that the selenium content of the ambient atmosphere in this area is simply the background amount that is present in the urban Birmingham atmosphere.

DETERMINATIONS OF Se(VI) WITH DAN

In further efforts to characterize the chemical forms in which selenium occurs in the ambient atmosphere, a question arose concerning the applicability of the DAN-fluorescence method of selenium analysis to the determination of selenium in the +6 oxidation state. Because the necessary oxidation state for DAN analysis is +4, it was considered important to determine if the method described by the Intersociety Committee for the selenium analysis of atmospheric particulate matter would account for any selenium present as selenate. Thus, experiments were conducted in our laboratories with known Se(VI) solutions (weighed as Na_2SeO_4) treated with the usual $HNO_3/HClO_4$ (10:1) digestion step, and subsequently analyzed by the DAN method. The results of these experiments are presented in Table 11. These results demonstrated that known Se(VI) solutions analyzed in the conventional manner gave essentially no indication of any selenium content; however, a known solution of Se(IV) analyzed simultaneously gave the expected result. Therefore, the results of a selenium analysis of a particulate sample containing selenate would have been expected to be low by the DAN method as it existed at that time. Consequently, additional experiments were directed toward finding a suitable reducing agent to incorporate in the DAN procedure. The proper reducing agent would ensure that all of the soluble selenium present as selenate would be reduced to selenite (Se(IV)) for reaction with DAN. A desirable reducing agent would also be compatible with the $HNO_3/HClO_4$ digestion mixture used to oxidize any elemental selenium that might be present in the particulate sample to Se(IV). The utility for this purpose of a hydrochloric acid digestion subsequent to the $HNO_3/HClO_4$ digestion was suggested by an article on the Se(IV)/Se(VI) electrochemical couple.[28] It was indicated in this study that the oxidation of Se(IV) to Se(VI) could be effected in aqueous solution with chlorine and that Se(VI) could in turn be reduced to Se(IV) by treatment with concentrated hydrochloric acid. Thus, a hydrochloric acid digestion step was incorporated in the analysis of known Se(VI) solutions by the DAN method. These results are also contained in Table 11. It was concluded that the hydrochloric acid digestion was effective in quantitatively reducing Se(VI) to Se(IV) for the DAN analysis. The final group of results in Table 11 indicate that the simultaneous determination of Se(IV) and Se(VI) was successful when the additional hydrochloric acid digestion was used but not when only the conventional $HNO_3/HClO_4$ digestion was used. In the latter case, only the selenium added as Se(IV) was determined and not the Se(VI). As a result of these findings, we included the hydrochloric acid digestion step in subsequent analyses of atmospheric particulate samples.

Table 11. EFFECT OF DIGESTION TREATMENT ON THE DETERMINATION OF SELENIUM BY THE DAN METHOD

Sample	Amount of Se taken, μg	Amount of Se found, μg	Digestion treatment
Se(IV) (control)	1.00	0.97	$HNO_3/HClO_4$
Se(VI)	1.00	<0.02	$HNO_3/HClO_4$
Se(VI)	0.75	<0.02	$HNO_3/HClO_4$
Se(VI)	0.50	<0.02	$HNO_3/HClO_4$
Se(IV) (control)	1.00	0.94	HCl
Se(VI)	1.00	0.95	HCl
Se(VI)	0.75	0.73	HCl
Se(VI)	0.50	0.52	HCl
Se(IV) (control)	1.00	0.96	H_2O only
Se(IV) + Se(VI)	0.5 + 0.5	0.97	$HNO_3/HClO_4$/HCl
Se(IV) + Se(VI)	0.5 + 0.5	0.50	$HNO_3/HClO_4$ only

ANALYSIS OF ATMOSPHERIC PARTICULATE MATERIAL FOR Se(VI)

These findings also suggested a means of estimating the relative amount of selenium present in a particulate sample as Se(VI). Consequently, we conducted selenium analyses of atmospheric particulate samples with and without the hydrochloric acid digestion step in an effort to determine whether Se(VI) was present in the samples. Although a limited number of determinations were made for this comparison, the results with the hydrochloric acid digestion step were not significantly different from those obtained without it; that is, the results of both methods agreed within the experimental reproducibility (2.0 ± 0.5 ng/m^3). On the basis of these limited findings, therefore, we may conclude that Se(VI) (as selenate) is not a primary form of atmospheric selenium.

ACCIDENTAL OXIDATION OF SELENIUM IN PARTICULATE MATERIAL TO Se(VI)

Particulate samples on glass-fiber filters that were treated with an extended $HClO_4/HNO_3$ digestion step and no hydrochloric acid digestion step appeared to contain essentially no selenium by conventional DAN analysis. However, an identical sample treated in the same manner but with the incorporation of the hydrochloric acid digestion step yielded the expected amount of selenium ($\sim$1.5 ng/m^3). The extended $HClO_4/HNO_3$ digestion step was characterized by the complete bleaching and dissolution of the initially black atmospheric particulate

matter by repeated heating to dense fumes of perchloric acid and to near dryness, whereas the usual $HClO_4/HNO_3$ digestion did not always result in complete dissolution of the particulate material because the samples were not taken to dense fumes of perchloric acid. It appeared that such rigorous oxidizing conditions may have oxidized all the selenium present in oxidation states lower than +6 to Se(VI). Subsequently, the sample treated with the hydrochloric acid digestion step gave the expected result because all the selenium that was previously oxidized to Se(VI) was reduced by the hydrochloric acid to Se(IV), the oxidation state appropriate for DAN analysis.

These apparently low results obtained in the case of an extended digestion with nitric and perchloric acids have been interpreted by other workers[29,30] to be due to losses of selenium by volatilization. The present results, however, suggest that the selenium was not lost at all but that it was simply oxidized to a form inappropriate for DAN analysis. Thus, the inclusion of a hydrochloric acid digestion step not only allows DAN determination of Se(VI), but it also minimizes the probability of low results due to over-oxidation in the $HClO_4/HNO_3$ digestion step.

SECTION IX

CONCLUSIONS CONCERNING THE NATURE OF ATMOSPHERIC SELENIUM

The statement is made in the description of the "Tentative Methods of Analysis for Selenium Content of the Atmospheric Particulate Matter" that "selenium may exist in the atmcsphere most probably as the element, the oxide, or as the selenite".[14] It is also stated that hydrogen selenide is likely to have a short lifetime because, like hydrogen sulfide, it is rapidly oxidized in air.

A similar conclusion can be drawn from the experimental evidence presented in this report. The present results indicate that the selenium contained in particulate matter consists of approximately equal amounts of water-soluble and water-insoluble forms of selenium. These forms are most likely elemental selenium as the water-insoluble form and selenium dioxide (or selenite) as the water-soluble form. Results of experiments designed to indicate the presence of Se(VI) failed to establish selenate as a component of atmospheric aerosols.

Results of experiments with the dry-selenium dioxide generator suggested that little or no selenium dioxide would exist as a true vapor in an ambient atmosphere. Indeed, it appears likely that atmospheric selenium dioxide exists as, or is associated with, particulate matter. These results also indicated that conventional particulate sampling would be sufficient for atmospheric selenium dioxide sampling with negligible losses due to volatilization. Experimental results also demonstrated the greater efficiency of glass-fiber filters relative to distilled-water bubblers for sampling the effluent of the dry-selenium dioxide generator. These observations and conclusions contradict statements by West as quoted in a recent article by Pupp et al.[31] West reported that gross sampling errors would occur for selenium dioxide if only particulate sampling was employed. Also, West suggested that bubblers filled with water are highly efficient samplers of selenium dioxide.

Pupp et al.[31] also reported a few measurements on the equilibbium vapor concentration of selenium dioxide. The method employed for the measurement was a weight-loss Knudsen system, which assumes a weight loss occurs because of the effusion of a vapor through an orifice. The values reported by Pupp

agree, in general, with the concentrations found in the effluent of the dry-selenium dioxide generator employed in this study. However, in the present work, it was found that the selenium dioxide existed almost entirely in an aerosol form and not in the expected vapor form.

Because the burning of fossil fuels, coal in particular, has been cited as the largest source of atmospheric selenium,[4] the chemical form of selenium emitted in this process is likely to be the predominant selenium species present in an ambient atmospheric aerosol. Recent studies have indicated that the selenium present in the effluent of a coal-burning power plant is exclusively in the elemental state.[32] It was suggested in these studies that the elemental selenium resulted from the reduction of selenium dioxide (or selenious acid) by sulfur dioxide. Also, it was determined that greater than 90% of the emitted selenium existed in the vapor phase. This result was observed in the case of a coal-burning steam plant with electrostatic precipitators that gave a fly-ash removal efficiency in excess of 99.5%.

However, it is possible, perhaps likely, that the elemental selenium vapor released from power plant stacks is converted rapidly to particulate form—by condensation or adsorption, or by some other process. This view was also presented by Weiss et al.[33] who studied selenium-to-sulfur ratios in dated Greenland ice cores and found that sulfur has increased considerably during recent times, whereas, selenium has remained fairly constant. Such results suggest that atmospheric selenium is particulate in nature and that input of elemental selenium vapor into the environment should be a local effect.

The manufacture of glass has also been pointed out as a significant source of atmospheric selenium.[4] At one location where large quantities of colored structural plate glass are produced, the stack effluent was analyzed. The stack effluent analysis showed that a large part of the metallic selenium used in the batch composition was volatilized during melting, and consequently appeared in the effluent as red, amorphous selenium metal. The particle size was reported to be less than 0.35 μm.[4]

The possibility of organic selenium compounds being present in the ambient atmosphere must at least be considered because of the metabolic fate of selenium ingested by both plants and animals. The volatile organic compound, dimethyl selenide, is an example of a selenium compound known to be a metabolic product expired by plants and animals.[17,18] Although this compound is one of the most probable forms of airborne organic selenium, the contribution of dimethyl selenide or any organic selenium compound to total atmospheric selenium in an urban

environment is likely to be very small. Indeed, no evidence for the presence of an organic selenium vapor—or any significant selenium vapor, for that matter—was obtained in this study. However, it should be pointed out that concentrations of elemental selenium vapor could have been underestimated in this investigation. Although the data of Pillay et al.[21,34] suggested that approximately 50% of atmospheric selenium is in a vapor form, bubblers used in the present study for atmospheric sampling indicated in one case a maximum of 20% selenium present in the vapor form.

Thus, it appears that the selenium present in the ambient atmosphere exists predominantly as, or in association with, particulate matter, and that atmospheric selenium is most likely in the chemical form of the element and the dioxide (or selenite).

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16. ABSTRACT

The primary purposes of this contract were to develop a collection technique for the quantitative collection of total atmospheric selenium and to characterize the forms in which selenium occurs in the atmosphere.

Retentive filters were used to collect particulate material containing selenium; chemically treated filters for the collection of gaseous or vaporous selenium were evaluated. Laboratory generators were setup for the evaluation of filter materials. The 2,3-diaminonaphthalene (DAN) fluorometric method was established as the primary analytical technique to determine selenium. Air particulate samples were analyzed for selenium and procedures were studied for determining relative amounts of selenium present in different oxidation states. Selenium aerosol and vapor generators were set up, characterized and used to evaluate other sampling devices.

Selenium appears to be present in ambient air predominantly as or with particulate matter; thus it was tentatively established that conventional particulate sampling suffices to collect the bulk of atmospheric selenium. Selenium vapors appear to make negligible contributions to total atmospheric selenium; however, concentrations of elemental selenium could have been underestimated.

The most probable chemical forms of atmospheric selenium were determined to be the element and the dioxide (or selenite).

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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